I. Introduction to Water Chemistry (1/2 week)
General Properties of Water
Composition of Different Waters
Methods of Expressing Concentrations
II. Chemical Equilibrium (1 week)
Thermodynamic Basis of Chemical Equilibrium
Enthalpy, Free Energy, and Equilibrium Constant
Non-ideal Behavior of Ions and Molecules in Solution
III. Chemical Kinetics (1 and 1/2 weeks)
Reaction Mechanism
Reaction Rate Laws
Temperature Effect on Reaction Rates
Catalysis
Empirical Rate Laws
IV. Acid-Base Chemistry (7 weeks)
Equilibrium Calculations * General Approaches
Mass Balance, Charge Balance, and Proton Condition
Equilibrium Relationships
Graphical Techniques for Equilibrium Calculations
Effects of Temperature and Ionic Strength on Equilibria
Mixtures of Acids and Base Calculations for pH Determination
pH Buffers and Buffer Intensity
Carbonate System and Its Equilibria
Alkalinity and Acidity
Theory of Acid-Base Titration
V. Precipitation and Dissolution (2 weeks)
Precipitation and Dissolution Kinetics
Equilibria of Dissolution
Solubility Product Concept
Temperature Effect on Solubility
Common Ion Effect
Complexation and Solubility
Solubility of Salts
Solubility Phase Diagrams and Their Applications
Ferrous and Ferric Carbonates and Hydroxides
Theoretical Aspects of Precipitation
VI. Oxidation-Reduction Reactions (1 week)
Redox Stoichiometry and Equilibria
Free Energy and Potential Half Reactions
Electrode Potential and the Nernst Equation
Electron Activity Concept
Equilibrium Calculations
Graphical Representation of Redox Equilibria
Applications of pe-pC and pe-pH Diagrams
Theories of Corrosion
Application of the Galvanic Cell Concept
Corrosion Control
Iron Chemistry and Acid Mine Drainage
Biologically Important Redox Reactions

BASIC WATER CHEMISTRY

The Properties of Water

Water is the most common substance known to man, as well as the most important. In vapor, liquid or solid form, water covers more than seventy percent of the Earth's surface, and is a major component of the atmosphere. Water is also an essential requirement for all forms of life. Most living things are largely made up of water. Human beings, for example, consist of about two-thirds water.

Pure water is a clear, colorless, and odorless liquid that is made up of one oxygen and two hydrogen atoms. The chemical formula of the water molecule, H_20, was defined in 1860 by the Italian scientist Stanislao Cannizzarro. Water is a very powerful substance that acts as a medium for many reactions, which is why it is often referred to as the "universal solvent." Although pure water is a poor conductor of electricity, impurities that occur naturally in water transform it into a relatively good conductor. Water has unusually high boiling (100° C/212° F) and freezing (0° C/32° F) points. It also shows unusual volume changes with temperature. As water cools, it contracts to a maximum density of 1 grain per cubic centimeter at 4° C (39° F). Further cooling actually causes it to expand, especially when it reaches the freezing point . The fact that water is denser in the liquid form than the solid form explains why an ice cube floats in a beverage, or why a body of water freezes from the top down. While the density property of water is of little importance to the beverage example, it has a tremendous impact on the survival of aquatic life inhabiting a body of water.

Ion Product Constant of Water

Water molecules are in continuous motion, even at lower temperatures. When two water molecules collide, a hydrogen ion is transferred from one molecule to the other *(Figure 1).* The water molecule that loses the hydrogen ion becomes a negatively charged hydroxide ion. The water molecule that gains the hydrogen ion becomes a positively charged hydronium ion. This process is commonly referred to as the *self ionization of water.*

° °
H–O + H–O **—>** H–O–H + H–O
| | |
H H H
Hydronium Hydroxide
Ion Ion

FIGURE 1 Self Ionization of Water

The self-ionization of water does not occur to a great extent. This reaction can be written as a simple dissociation *(Figure 2).* At 25°C in pure water, each concentration of hydrogen ions and hydroxide ions is only 1×10^{-7} M. It is important to note that the amounts of hydrogen and hydroxide ions produced from this reaction are equal. This is why pure water is often described as a *neutral solution.*

$H_2O \underset{<-}{->} H^+ + OH^-$

Hydrogen Hydroxide
Ion Ion
FIGURE 2 Dissociation of Water
In all other aqueous solutions, the relative concentrations of each of these ions are unequal. When more of one ion is added to the solution, the concentration of the other decreases. The following equation describes this relationship:
$[H^+] [OH^-] = I \times 10^{-14} (mol/L)^2 = K_w$
The product of the hydrogen and hydroxide ions is always equal to I x 10-^{14} $(mol/L)^{-14}$. Therefore, if the concentration of one ion increases by a factor of 10, then the concentration of the other ion must decrease by a factor of 10. Since this relationship is constant, it is given the symbol K_w, which is called the *ion-product for water.*
Aqueous solutions that have a hydrogen ion concentration greater than the hydroxide ion concentration are called *acidic solutions***.** When the hydroxide ion concentration is greater than the hydrogen ion concentration, the solution is called *basic* or *alkaline.*
Molarity
The term "molarity" is used to describe the concentration of a substance within a solution. By definition, a one "molar" solution of hydrogen ion contains one "mole" of hydrogen ion per liter of solution. Therefore, a solution of 10 pH has 1 x 10^{-10} moles of hydrogen ions as shown by the following equation:
1×10^{-10}mol=1 x 10-10g hydrogen ion
1L
Furthermore, a solution of 4 pH has 1 x 10^{-4} moles of hydrogen ions, and so on. This also means that one liter of a pH 10 solution would contain 1 x 10^{-10} grams of hydrogen ion, because I mole=1 g/L for hydrogen.
A one molar solution of sodium hydroxide (NaOH), a base, is approximately 4% by weight, and has a pH value of 14. A one molar solution of hydrochloric acid (HCI), an acid, is approximately 3.7% by weight, and has a pH of 0. By diluting either of these two solutions, the molarity will decrease as well. For example, diluting 1 ml of HCI acid by adding 9 ml of distilled water results in a 0. I molar hydrochloric acid solution which has a pH value of 1.0. Diluting sodium hydroxide using the same volumes yields a solution with a pH value of 13. If this dilution procedure was continued, the pH of each solution would approach a neutral pH of 7.
NOTE: For every 10- foId change in
concentration (example: 0. I to 1. 0),
the pH Changes by one unit.
If equal volumes of 4 pH (0.0001M HCI) and 10 pH (0.0001 NaOH) solutions were mixed together, the resultant solution would have a pH of 7.
NOTE: HCI and NaOH having opposing
$[H^+]$/[OH] concentrations.
The same result would apply when mixing equal volumes of a 6 pH acid and an 8 pH base, a 2 pH acid and a 12 pH base, and so on.